INVESTIGATION OF ALUM MIXTURES FOR THE REMOVAL AND DECONTAMINATION V AND G TYPE CHEMICAL WARFARE AGENTS FROM AQUEOUS SOLUTIONS

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ABSTRACT

Truly environmentally friendly means of detoxifying chemical warfare agents have yet to be developed. Toward this end, Soman (GD), VX and agent simulants were treated with aqueous aluminum sulfate (alum), sodium aluminate, or mixtures of the two. The mixtures were prepared by combining varying volumes of the aqueous salts to give buffered solutions (pH 2-12). Reactions were tracked using phosphorus-31 nuclear magnetic resonance (NMR) and gas chromatography/mass spectrometry (GC/MS). Simulants studied were triethylphosphate (TEP), tributylphosphate (TBP), diisopropylphosphorofluoridate (DPF), O,O'-dimethylmethyl phosphonate (DMMP), and malathion. Saturated alum alone removed approximately 10%, 20%, and 94% of DMMP, TBP, and TEP, respectively, upon immediate mixing. The buffered alum solutions formed a flocculent aluminum hydroxide precipitate upon reaction, which was effective to varying degrees in removing or chemically altering simulants depending on pH. A basic buffer at pH 12.3 and an acidic buffer at pH 3.8 were used for most of the studies. Malathion was decomposed within 4 days by the basic buffer, but remained unreacted in the acidic buffer. VX was unaffected by the acidic buffer. GD was eliminated from the aqueous acidic buffer within 18 hours, with nearly 60% removed within the first 10 minutes. GC/MS confirmed that, after 24 hours, a chloroform extract of the precipitate formed by this GD reaction contained less than 4% of the original GD. Studies are continuing, but it appears that alum buffers may provide an effective alternate method for the destruction of G type nerve agents.

INTRODUCTION

Recent media attention has focused on the challenges and anxiety associated with chemical warfare agent (CWA) destruction and disposal which is viewed by some as a potential public health menace.[1,2] Truly environmentally friendly means of detoxifying chemical warfare agents have yet to be developed, and the possibility of using alum and alum mixtures may be one feasible attractive alternative. Alum (aluminum sulfate) and alum mixtures have a long history of usage by municipal water treatment facilities as coagulants in the purification and finishing of

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drinking water. Alum and alum buffered by the addition of sodium aluminate have even been used by lake managers for phosphate removal from lakes and reservoirs that were impacted by excess nutrient input giving rise to unwanted algal blooms.[3] It was these large scale applications that led us to look further into the possibility of using alum and alum mixtures as alternatives for the destruction of stockpiles of CWA's, particularly the V- and G-class nerve agents. It is well known that G- and V-type nerve agents hydrolyze under a variety of conditions, and hydrolysis kinetics have been studied for many of these CWA's. [4,5,6] The pH of alum and alum mixtures can be widely varied from strongly acidic to strongly basic depending on concentrations and proportions of components, which should allow for some control over hydrolysis rates. Thus it was thought that they would have great potential in not only hydrolyzing the agents, but also in rendering the phosphate by-products inactive in the resultant coagulant floc that forms. Here, we report the first installment of an investigation of the potential of using alum and alum mixtures for the destruction of V- and G-type chemical stockpiles. These investigations include work on both simulants and agents.

EXPERIMENTAL

Solutions of aluminum sulfate (alum) and sodium aluminate buffer mixtures were prepared in either 2.0 mL microfuge tubes or 10.0 mL Pyrex test tubes and diluted with deionized (DI) water. Two series were prepared: one by combining saturated solutions of the two reagents, another by mixing 1.0 M solutions. All were brought up to a constant total volume, and pH was measured using a Scientific Instruments IQ150 pH Meter fitted with solid state pH probe with internal reference. Volume fractions of alum relative to the sum of alum plus sodium aluminate volumes were then computed and plotted against pH as seen in Figure 1. Estimated error in reported pH values is ±0.5 units. In the case of the saturated solutions, the molar values are estimated to be 1.2 M for aluminum sulfate and 4.8 M for sodium aluminate.

Both VX and GD were obtained from the Chemical Transfer Facility. The purity of both agents was deemed satisfactory for study based on ^{31}P Nuclear Magnetic Resonance (NMR) spectra collected in $CDCl_3$ as described below. All chemicals were used as commercially obtained (Aldrich and subsidiaries) without further purification. Solutions of 1.0 M $Al_2(SO_4)_3$, 1.0 M $NaAlO_2$, saturated $Al_2(SO_4)_3$ (ca. 50% by weight)[7], and saturated $NaAlO_2$ (ca. 30% by weight)[8] were all prepared with DI water. Unless otherwise noted, all reactions were carried out in 5 mm NMR tubes (507-PP Wilmad Glass, Inc.) in total volumes ranging from 700 μL to 1000 μL. The total volumes include D_2O added as a lock solvent to give between 3% to 30% D_2O by volume. Proton decoupled ^{31}P NMR spectra were collected on samples prepared directly in NMR tubes as described above using a Bruker AVANCE 300 MHz NMR spectrometer fitted with 5mm broadband probe. All spectra were referenced to external H_3PO_4 (1% (v/v) in D_2O; 0 ppm). Test solutions were prepared by adding from 20 μL to 200 μL simulant/agent to NMR tubes already containing D_2O and H_2O. Alum solutions were then added and the reaction components mixed using a vortex mixer (Fisher Scientific). All reactions were carried out at ambient temperature which ranged from 21° to 23° C and initial spectra were collected within one hour after mixing unless otherwise noted. Chemical shifts are reported in ppm (δ) relative to the external H_3PO_4 standard. The signal detection limit for ^{31}P NMR is calculated to be at 0.1% of the original agent/simulant concentration.

GC/MS experiments were carried out on $CHCl_3$ extracts of the GD agent samples. After the reactions went to completion as judged from the NMR analyses, precipitates of the NMR samples were extracted using 0.5 mL of $CHCl_3$. They were analyzed using a JEOL GCmate II mass

spectrometer operated at low mass resolution and 70 eV electron impact ionization. Quantitation was done by comparison to external standards of GD run under the same conditions.

Timed experiments on simulants/agents were performed on samples prepared as described above to monitor loss of reactant from the solution over time. Values for pH in the reaction rate experiments were estimated based on the solution composition and the pH of the mixtures described above. Reactivity is reported as the percentage of unreacted simulant/agent as calculated using the NMR peak area relative to either the peak area of an internal standard (hexamethylphosphoramide, HMPA), or relative to the peak area of a blank simulant/agent standard made without the alum buffer added. For each spectrum, the reaction time was taken to be the midpoint of the data acquisition period of 10.2 minutes. Initial spectra were obtained within the first fifteen minutes after mixing. Error bars represent the 95% confidence limits (α = 0.025) based on multiple measurements of peak area.

RESULTS AND DISCUSSION

The original goal behind this research was to determine if alum and alum buffer mixtures could, in addition to hydrolyzing various nerve agents, also completely remove the hydrolysis product(s) from solution. Hence, we first analyzed the efficiency of specific alum mixtures at removing phosphoric acid itself as well as two simple organophosphate esters, triethyl phosphate (TEP) and tributyl phosphate (TBP). Three phosphoric acid samples (200 µL) were tested with: 1) 500 µL of 1.0 M $Al_2(SO_4)_3$, 2) a mixture of 250 µL each of 1.0 M $Al_2(SO_4)_3$ and 1.0 M $NaAlO_2$ (to be called "acidic buffered alum" or ABA from here on), and 3) 500 µL of 1.0 M $NaAlO_2$. ABA was the only mixture of the three that produced a heavy flocculant precipitate upon mixing. In all three cases, the ^{31}P signal disappeared indicating the removal of the phosphate species from solution. Both organophosphate esters (20 µL) were treated similarly, and Table 1 shows the results. Additionally, both TBP and TEP were treated with a large molar excess of saturated aluminum sulfate solution by placing 100 µL of each simulant into 3000 µL of the sulfate solution. As can be seen from Figure 1, the alum buffer mixtures can be prepared to cover a wide range of pH values whether prepared from 1.0 M reagents or saturated solutions. For stock solutions, we chose 1.0M concentrations to be able to more accurately control the mole fraction of each component added, and saturated solutions to provide excess reagent if needed. The figure shows pH as a function of volume fraction of alum in the mixture.
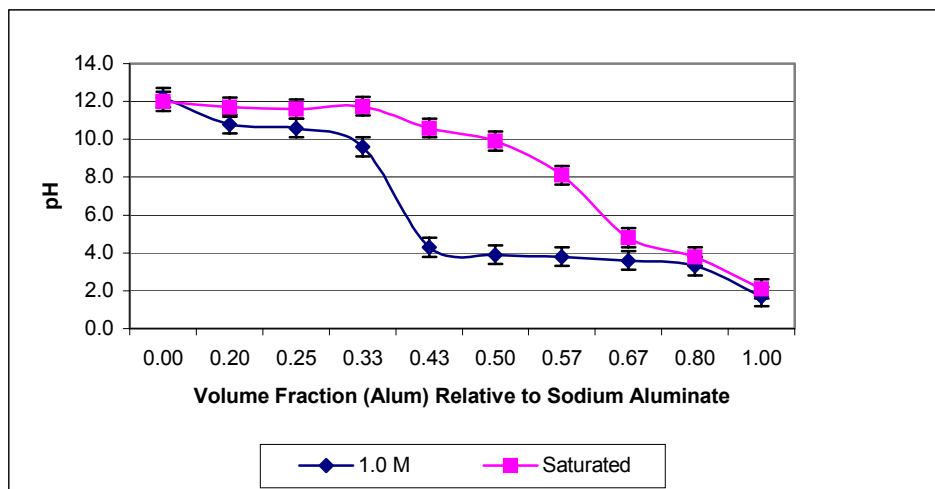

Figure 1: Alum buffer pH graph as a function of volume fraction

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Phosphate Simulants

All three of the alum mixtures were expected to remove the phosphoric acid since reactions would result in the precipitation of $AlPO_4$ in all cases. Saturated alum appeared to be the most efficient for removing TEP from solution, but the least efficient for TBP. This may be the result of a combination of ease of hydrolysis and simulant solubility differences in a solution of high ionic strength such as saturated alum. TBP tends to be less soluble in aqueous solutions than TEP.[7] Our attention was drawn to the acidic buffered alum (ABA) solution because of the floc that was formed upon mixing. Despite the fact that it was not as effective for TEP at least for an immediate reaction, it was effective on TBP, and the floc could potentially help entrain byproducts as well as unreacted simulants/agents. Thus, this was the mixture of choice in doing experiments on agents as reported below.

TABLE 1.   % Simulant remaining after addition of various alum mixtures

	0.70 M* $Al_2(SO_4)_3$	0.70 M* $NaAlO_2$	ABA (pH 3.8)	Saturated Alum
H_3PO_4	0	0	0	NT
TEP	36.6 ±0.2**	61.1 ±0.6	72.0 ±3.8	6.3 ±0.1
TBP	9.3 ±0.8	2.5 ±0.5	0	79.1 ±1.2
DMMP	NT	NT	48.2 ±0.2	88.2 ±3.2

*Concentration of 1.0 M reagents after dilution

**95% C.L.

NT - not tested
Key: TBP - Tributyl phosphate; TEP - Triethyl phosphate;
DMMP - O,O'-dimethyl methylphosphonate; ABA - acidic buffered alum.

A reation rate study was carried out on the treatment of TBP with ABA. Figure 2 shows the results of tracking the decomposition of TBP in a solution prepared by adding 100 μL each of 1.0 M $Al_2(SO_4)_3$ and 1.0 M $NaAlO_2$ to the 50 μL (ca. 50 mg) simulant in 350 μL of H_2O and 100 μL of D_2O. The more dilute mixture was chosen for two reasons. First, if the reaction mechanism were controlled by the concentration of aluminum in solution, the overall reaction would be slower thus allowing it to be more easily tracked over a longer period of time. Secondly, it was noted that the precipitate was thicker and more difficult to work with for the more concentrated ABA, especially in a 5 cm NMR tube. The mole ratio of Al to simulant in the dilute ABA buffer is approximately 1.6:1, and in the more concentrated ABA reported in Table 1, it is about 10:1.

As can be seen in Figure 2, the curve does not fit any of the classical kinetic models, which is not surprising since the reaction mixture is very heterogeneous despite the lower concentration of buffer used. Low signal to noise ratio in the spectra gave rise to a large variability in the integration values, accounting for the large error bars. This was the case in all reaction rate studies done in NMR tubes with either simulant or agent. Issues of incomplete mixing and settling of the precipitate during spinning in the probe made for non-ideal conditions. Nevertheless, it can be seen that despite theses challenges, the simulant was totally removed (below detection limits of 0.1%) from solution within 18 hours.
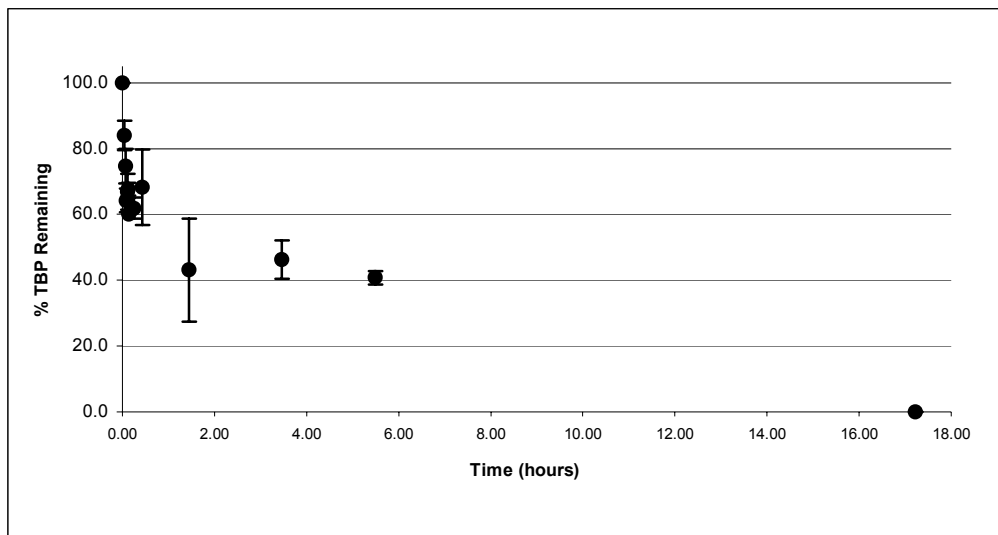
Figure 2: Decomposition of tributyl phosphate in acidic buffered alum solution.

Phosphonate Simulants

As can be seen in Table 1, the acidic buffered alum solution was more successful in reducing the concentration of DMMP than saturated alum. Subsequent reaction rate studies with ABA on DMMP, however, showed no further significant reduction in concentration over time. Work by Brevett and Wagner[9] shows that DMMP is more effectively hydrolyzed at higher pH. Whether DMMP was actually hydrolyzed and precipitated or simply taken out of solution by surface adsorption to the floc is unknown at this time. Since the alum buffer system has flexibility with regard to pH, we decided to switch to a strongly basic buffer (pH 12.3) using the saturated stock solutions. Figure 3 shows the results of a reaction rate study in which the DMMP peak (δ 38.4 ppm) was gone in approximately one hour. In addition to the disappearance of DMMP from solution, as can be seen in Figure 3, the strongly basic alum buffer removes about 50% of all DMMP products over the time frame studied and produces the monosodium salt of O-methyl methylphosphonic acid (NaMMP). There is NMR evidence that the disodium salt of methylphosphonic acid is also produced.
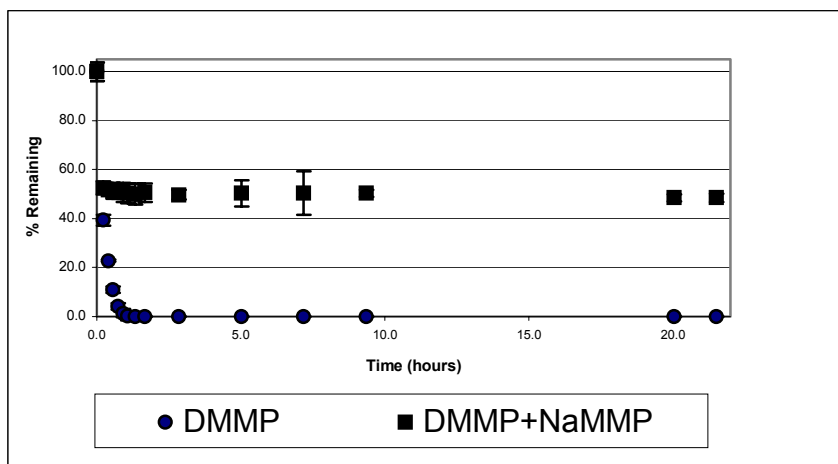

Figure 3. Decomposition of DMMP in strong basic buffered alum.

Agent Studies

Two agents were chosen for study, VX (O-ethyl S-[2-(diisopropylamino)ethyl] methylphosphonothioate and GD (Soman or 3,3-dimethyl-2-butylmethylphosphono-fluoridate). Both were tested with acidic buffered alum only. The GD reaction was carried out twice, once with an external standard in water and once with an HMPA internal standard. The average results of the two time studies are seen in Figure 4. The ^{31}P NMR signal for GD was below detection limits within eighteen hours of treatment. Furthermore, GC/MS chloroform extracts of the reaction precipitate recovered about 3%-5% of the initial GD indicating that 95%-97% had been destroyed or had been turned into product not extractable with chloroform. On average, about 60% of the GD is gone within the first ten minutes. No other hydrolysis products were identified in the GC/MS spectrum indicating at least that the hydrolysate is associated with the floc. One would expect that the fluoride may form the very stable hexafluoroaluminate(III) anion, but this remains unconfirmed.
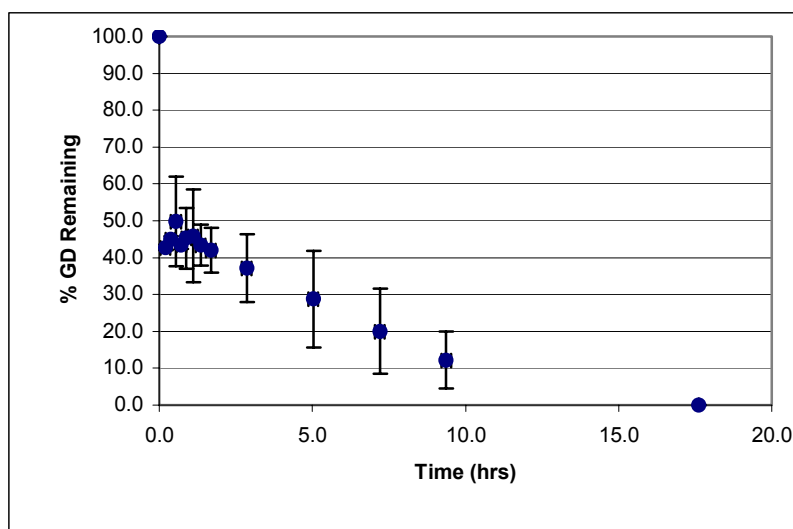

Figure 4. Decomposition of GD in acidic buffered alum solution.

VX, on the other hand, did not respond to the acidic buffer. This time, however, an initial standard in water was not measured and an internal standard was not used for the reaction rate study, so the amount of VX that precipitated in the floc was not determined. Based on the observed reaction of the remaining agent, however, it was evident that the destruction of VX in this solution was not efficient. It was expected that the acidic buffer would be more effective than the basic buffer simply because VX is more soluble in acid than in base.[4] However, the ^{31}P spectrum VX peak at δ 63.3 ppm showed no decrease in size over twenty four hours. The acidic floc was therefore ineffective at removing the agent from solution. An additional 100 μL of saturated NaAlO$_2$ was added to the NMR tube to bring the pH up to what was estimated to be around 12, and the reaction was checked periodically over another five days. The final measurement showed only a loss of about 25% of the VX after the addition of NaAlO$_2$. Clearly the VX is resistant to either the acidic or basic alum buffer. Also, the acidic buffered alum had no effect on malathion. On the other hand, similar to DMMP, malathion was altered in strongly basic buffer with the main peak decreasing in area over time and two new peaks increasing in area. The identity of the decomposition products for malathion has yet to be determined, but it is clear that a new strategy must be employed for V-type agents and simulants.

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CONCLUSIONS

These studies have shown that alum buffer mixtures are effective at removing certain phosphoryl-based simulants and nerve agents from water. In addition, the kinetics of hydrolysis can be controlled to some degree by adjusting the molar ratio of alum relative to simulant/agent. The specific alum mixture used must be optimized for each compound individually if the most efficient removal of that compound and its byproducts is desired. Thus, these studies with buffered alum solutions on both simulants and agents have demonstrated a promising technology for the decomposition and removal of G agents. The approach may be effective for precipitating the hydrolysis products of V agents if appropriate hydrolysis conditions can be developed for the aqueous phase. There are still many unanswered questions which need investigation before implementing this technology. Proposed future work will involve identification of decomposition products in the alum floc and supernatant solution, particularly for agent work, since it must be demonstrated that both floc and hydrolysate are non-toxic when they are introduced into landfills and waste streams respectively. Alum buffers had only a marginal effect on malathion and VX, which is an agent of major concern regarding its destruction.[2] It is possible that different stoichiometries of alum buffer could prove useful, but an alternate processes should also be investigated. Nevertheless, this work has demonstrated that alum buffers may be effectively used on destroying stockpiles of GD and perhaps other G type CWA's.

This approach may be developed further to insure the safety of municipal drinking water supplies. Since alum is already used for water purification, the optimization of the filtering conditions may be necessary to purify water in the event that a water supply is contaminated by CW agents in an accidental spill or a terrorist incident.

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